

U.S. Patent Application Serial No. 09/895,331  
Response filed January 4, 2005  
Reply to OA dated October 5, 2004

**AMENDMENTS TO THE CLAIMS:**

Please cancel claims 2 and 5 without prejudice or disclaimer. Please amend claim 1 and add new claims 8-16 as follows:

**Claim 1 (Currently amended):** An aqueous dry laminate adhesive composition for artificial leather comprising:

a water-borne polyurethane resin (A), a crosslinking agent (B), and a thickener (C), and colorant (D);

wherein said water-borne polyurethane resin (A) has a weight-average molecular weight ranging from 2,000 to 200,000 and has a hydrophilic group and at least two active hydrogen atom containing groups, which are reactive with isocyanate groups and are selected from the group consisting of a carboxyl group, a hydroxyl group, and an amino group, and a content of said hydrophilic groups in the water-borne polyurethane resin (A) is at least 0.005 to 0.2 equivalent per 100 parts by weight of the finally obtained polyurethane resin, and said water-borne polyurethane resin (A) has a softening temperature of less than 50 °C and a viscosity of the melt at 50 °C of less than 10<sup>5</sup> Pa·s, and

wherein a softening temperature of a cured product obtained after curing a reaction product between said water-borne polyurethane resin (A) and the crosslinking agent (B) is higher than 120 °C,

wherein said crosslinking agent (B) is a polyisocyanate compound crosslinking agent, and said thickener (C) is a surface active agent in the system of an association polymer an association

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polymer surface active agent, and said colorant (D) is a water dispersible pigment in which a pigment's surface is coated with a water disperible resin, and

wherein said water-borne polyurethane resin (A) is a polyurethane resin obtained by one of:

(1) a method comprising the steps of preparing an organic solvent solution of a polyurethane resin containing carboxyl groups, by reacting a compound containing active hydrogen atoms and a compound containing carboxyl groups with polyisocyanate, and then optionally adding a nonionic emulsifier and a neutralizer to the organic solvent solution or an organic solvents dispersion and obtaining an aqueous dispersion of the water-borne polyurethane resin by mixing the above-described solution containing additives with water,

(2) a method comprising the steps of preparing a polyurethane prepolymer containing carboxyl groups and containing isocyanate groups at the terminal ends of the prepolymer, by reacting a compound containing active hydrogen atoms and a compound containing carboxyl groups with isocyanate, optionally mixing the prepolymer with an aqueous solution containing a nonionic emulsifier and a neutralizer or adding a neutralizer in advance to the urethane prepolymer, dispersing the urethane prepolymer in the aqueous solution containing a nonionic emulsifier, and obtaining an aqueous dispersion by reacting polyamine with polyisocyanate groups including the prepolymer,

(3) a method comprising the steps of preparing a polyurethane resin containing hydrophilic groups by reaction of a compound containing active hydrogen atoms and a compound containing carboxyl groups with isocyanate, preparing an organic solvent solution or an organic solvent dispersion of the polyurethane resin, and obtaining an aqueous dispersion by optionally mixing the

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above organic solution and water with an addition of a neutralizer,

(4) a method comprising the steps of preparing a polyurethane prepolymer containing carboxyl groups and isocyanate groups at the terminal ends of a prepolymer, by reacting a compound containing active hydrogen atoms and a compound containing carboxyl groups with isocyanate, mixing the prepolymer with an aqueous solution containing a neutralizer, or adding a neutralizer to the prepolymer, and mixing with water, and further adding a polyamine for obtaining an aqueous dispersion, and

(5) a method comprising the steps of preparing a polyurethane prepolymer containing carboxyl groups and containing isocyanate groups at terminal ends of the prepolymer, by reacting a compound containing active hydrogen atoms and a compound containing carboxyl groups with isocyanate, mixing with an aqueous solution containing a neutralizer and polyamine, or adding a neutralizer to the prepolymer beforehand, and mixing with an aqueous solution containing polyamine for obtaining an aqueous dispersion.

**Claims 2-5 (Canceled).**

**Claim 6 (Withdrawn):** A method of manufacturing artificial leather comprising the steps of:

forming an adhesive layer by coating said aqueous dry laminate adhesive composition according to claim 1 on a skin layer of the artificial leather formed beforehand on the release paper;

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and

bonding said adhesive layer with a base fabric material of a artificial leather by a dry laminate process.

**Claim 7 (Withdrawn):** Artificial leather products which are obtained by the manufacturing method according to claim 6.

**Claim 8 (New):** An aqueous dry laminate adhesive composition for artificial leather comprising:

a water-borne polyurethane resin (A), a crosslinking agent (B), and a thickener (C);  
wherein said water-borne polyurethane resin (A) has a weight-average molecular weight ranging from 2,000 to 200,000 and has a hydrophilic group and at least two active hydrogen atom containing groups, which are reactive with isocyanate groups, and a content of said hydrophilic groups in the water-borne polyurethane resin (A) is at least 0.005 to 0.2 equivalent per 100 parts by weight of the finally obtained polyurethane resin, and said water-borne polyurethane resin (A) has a softening temperature of less than 50°C and a viscosity of the melt at 50°C of less than 10<sup>5</sup> Pa · s;

wherein a softening temperature of a cured product obtained after curing a reaction product between said water-borne polyurethane resin (A) and the crosslinking agent (B) is higher than 120°C;

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wherein the crosslinking agent (B) is a polyisocyanate compound, and said thickener (C) is an association polymer surface active agent; and

wherein said water-borne polyurethane resin (A) is a polyurethane resin obtained by one of:

- (1) a method comprising the steps of preparing an organic solvent solution of a polyurethane resin containing carboxyl groups, by reacting a compound containing active hydrogen atoms and a compound containing carboxyl groups with polyisocyanate, and then optionally adding a nonionic emulsifier and a neutralizer, to the organic solvent solution or an organic solvents dispersion and obtaining an aqueous dispersion of the water-borne polyurethane resin by mixing the above-described solution containing additives with water,
- (2) a method comprising the steps of preparing a polyurethane prepolymer containing carboxyl groups and containing isocyanate groups at the terminal ends of the prepolymer, by reacting a compound containing active hydrogen atoms and a compound containing carboxyl groups with isocyanate, optionally mixing the prepolymer with an aqueous solution containing a nonionic emulsifier and a neutralizer or adding a neutralizer in advance to the urethane prepolymer, dispersing the urethane prepolymer in the aqueous solution containing a nonionic emulsifier, and obtaining an aqueous dispersion by reacting polyamine with polyisocyanate groups including the prepolymer,
- (3) a method comprising the steps of preparing a polyurethane resin containing hydrophilic groups by reaction of a compound containing active hydrogen atoms and a compound containing carboxyl groups with isocyanate, preparing an organic solvent solution or an organic solvent dispersion of the polyurethane resin, and obtaining an aqueous dispersion by optionally mixing the above organic

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solution and water with addition of a neutralizer,

(4) a method comprising the steps of preparing a polyurethane prepolymer containing carboxyl groups and isocyanate groups at the terminal ends of the prepolymer, by reacting a compound containing active hydrogen atoms and a compound containing carboxyl groups with isocyanate, mixing the prepolymer with an aqueous solution containing a neutralizer, or adding a neutralizer to the prepolymer, and mixing with water, and further adding a polyamine for obtaining an aqueous dispersion, and

(5) a method comprising the steps of preparing a polyurethane prepolymer containing carboxyl groups and containing isocyanate groups at terminal ends of the prepolymer, by reacting a compound containing active hydrogen atoms and a compound containing carboxyl groups with isocyanate, mixing with an aqueous solution containing a neutralizer and polyamine, or adding a neutralizer to the prepolymer beforehand, and mixing with an aqueous solution containing polyamine for obtaining an aqueous dispersion.

**Claim 9 (New):** An aqueous dry laminate adhesive composition for artificial leather according to claim 8, wherein the active-hydrogen-atom containing groups are selected from the group consisting of a carboxyl group, a hydroxyl group, and an amino group.

**Claim 10 (New):** An aqueous dry laminate adhesive composition for artificial leather according to claim 8, wherein the aqueous dry laminate adhesive composition further comprises a

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colorant (D) which is a water dispersible pigment in which a pigment's surface is coated with a water dispersible resin.

**Claim 11 (New):** An aqueous dry laminate adhesive composition for artificial leather comprising:

a water-borne polyurethane resin (A), a crosslinking agent (B), a thickener (C), and colorant (D);

wherein said water-borne polyurethane resin (A) has a weight-average molecular weight ranging from 2,000 to 200,000 and has a hydrophilic group and at least two active hydrogen atom containing groups, which are reactive with isocyanate groups, and said water-borne polyurethane resin (A) has a softening temperature of less than 50°C and a viscosity of the melt at 50°C of less than  $10^5$  Pa • s;

wherein a softening temperature of a cured product obtained after curing a reaction product between said water-borne polyurethane resin (A) and the crosslinking agent (B) is higher than 120°C;

wherein said crosslinking agent (B) is a polyisocyanate compound, and said thickener (C) is an association polymer surface active agent, and said colorant (D) is a water dispersible pigment in which a pigment's surface is coated with a water dispersible resin; and

wherein said water-borne polyurethane resin (A) is a polyurethane resin polyurethane resin obtained by one of:

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- (1) a method comprising the steps of preparing an organic solvent solution of a polyurethane resin containing carboxyl groups, by reacting a compound containing active hydrogen atoms and a compound containing carboxyl groups with polyisocyanate, and then optionally adding a nonionic emulsifier and a neutralizer, to the organic solvent solution or an organic solvents dispersion and obtaining an aqueous dispersion of the water-borne polyurethane resin by mixing the above-described solution containing additives with water,
- (2) a method comprising the steps of preparing a polyurethane prepolymer containing carboxyl groups and containing isocyanate groups at the terminal ends of the prepolymer, by reacting a compound containing active hydrogen atoms and a compound containing carboxyl groups with isocyanate, optionally mixing the prepolymer with an aqueous solution containing a nonionic emulsifier and a neutralizer or adding a neutralizer in advance to the urethane prepolymer, dispersing the urethane prepolymer in the aqueous solution containing a nonionic emulsifier, and obtaining an aqueous dispersion by reacting polyamine with polyisocyanate groups including the prepolymer,
- (3) a method comprising the steps of preparing a polyurethane resin containing hydrophilic groups by reaction of a compound containing active hydrogen atoms and a compound containing carboxyl groups with isocyanate, preparing an organic solvent solution or an organic solvent dispersion of the polyurethane resin, and obtaining an aqueous dispersion by optionally mixing the above organic solution and water with addition of a neutralizer,
- (4) a method comprising the steps of preparing a polyurethane prepolymer containing carboxyl groups and isocyanate groups at the terminal ends of the prepolymer, by reacting a compound

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containing active hydrogen atoms and a compound containing carboxyl groups with isocyanate, mixing the prepolymer with an aqueous solution containing a neutralizer, or adding a neutralizer to the prepolymer, and mixing with water, and further adding a polyamine for obtaining an aqueous dispersion, and

(5) a method comprising the steps of preparing a polyurethane prepolymer containing carboxyl groups and containing isocyanate groups at terminal ends of the prepolymer, by reacting a compound containing active hydrogen atoms and a compound containing carboxyl groups with isocyanate, mixing with an aqueous solution containing a neutralizer and polyamine, or adding a neutralizer to the prepolymer beforehand, and mixing with an aqueous solution containing polyamine for obtaining an aqueous dispersion.

**Claim 12 (New):** An aqueous dry laminate adhesive composition for artificial leather according to claim 11, wherein the active-hydrogen-atom containing groups are selected from the group consisting of a carboxyl group, a hydroxyl group, and an amino group.

**Claim 13 (New):** An aqueous dry laminate adhesive composition for artificial leather according to claim 11, wherein a content of the hydrophilic groups in the water-borne polyurethane resin (A) is at least 0.005 to 0.2 equivalent per 100 parts by weight of the finally obtained polyurethane resin.

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**Claim 14 (New):** An aqueous dry laminate adhesive composition for artificial leather comprising:

a water-borne polyurethane resin (A), a crosslinking agent (B), and a thickener (C);

wherein said water-borne polyurethane resin (A) has a weight-average molecular weight ranging from 2,000 to 200,000 and has a hydrophilic group and at least two active hydrogen atom containing groups, which are reactive with isocyanate groups and are selected from the group consisting of a carboxyl group, a hydroxyl group, and an amino group, and said water-borne polyurethane resin (A) has a softening temperature of less than 50°C and a viscosity of the melt at 50°C of less than  $10^5$  Pa • s;

wherein a softening temperature of a cured product obtained after curing a reaction product between said water-borne polyurethane resin (A) and the crosslinking agent (B) is higher than 120°C;

wherein said crosslinking agent (B) is a polyisocyanate compound, and said thickener (C) is an association polymer surface active agent; and

wherein said water-borne polyurethane resin (A) is a polyurethane resin obtained by one of:  
(1) a method comprising the steps of preparing an organic solvent solution of a polyurethane resin containing carboxyl groups, by reacting a compound containing active hydrogen atoms and a compound containing carboxyl groups with polyisocyanate, and then optionally adding a nonionic emulsifier and a neutralizer, to the organic solvent solution or an organic solvents dispersion and obtaining an aqueous dispersion of the water-borne polyurethane resin by mixing the above-

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described solution containing additives with water,

- (2) a method comprising the steps of preparing a polyurethane prepolymer containing carboxyl groups and containing isocyanate groups at the terminal ends of the prepolymer, by reacting a compound containing active hydrogen atoms and a compound containing carboxyl groups with isocyanate, optionally mixing the prepolymer with an aqueous solution containing a nonionic emulsifier and a neutralizer or adding a neutralizer in advance to the urethane prepolymer, dispersing the urethane prepolymer in the aqueous solution containing a nonionic emulsifier, and obtaining an aqueous dispersion by reacting polyamine with polyisocyanate groups including the prepolymer,
- (3) a method comprising the steps of preparing a polyurethane resin containing hydrophilic groups by reaction of a compound containing active hydrogen atoms and a compound containing carboxyl groups with isocyanate, preparing an organic solvent solution or an organic solvent dispersion of the polyurethane resin, and obtaining an aqueous dispersion by optionally mixing the above organic solution and water with addition of a neutralizer,
- (4) a method comprising the steps of preparing a polyurethane prepolymer containing carboxyl groups and isocyanate groups at the terminal ends of the prepolymer, by reacting a compound containing active hydrogen atoms and a compound containing carboxyl groups with isocyanate, mixing the prepolymer with an aqueous solution containing a neutralizer, or adding a neutralizer to the prepolymer, and mixing with water, and further adding a polyamine for obtaining an aqueous dispersion, and
- (5) a method comprising the steps of preparing a polyurethane prepolymer containing carboxyl

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groups and containing isocyanate groups at terminal ends of the prepolymer, by reacting a compound containing active hydrogen atoms and a compound containing carboxyl groups with isocyanate, mixing with an aqueous solution containing a neutralizer and polyamine, or adding a neutralizer to the prepolymer beforehand, and mixing with an aqueous solution containing polyamine for obtaining an aqueous dispersion.

**Claim 15 (New):** An aqueous dry laminate adhesive composition for artificial leather according to claim 14, wherein the aqueous dry laminate adhesive composition further comprises a colorant (D) which is a water dispersible pigment in which a pigment's surface is coated with a water dispersible resin.

**Claim 16 (New):** An aqueous dry laminate adhesive composition for artificial leather according to claim 14, wherein a content of said hydrophilic groups in the water-borne polyurethane resin (A) is at least 0.005 to 0.2 equivalent per 100 parts by weight of the finally obtained polyurethane resin.